# Interfacial Processes in EES Systems
# Advanced Diagnostics


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2019 Annual Merit Review

June 10-13, 2019

Project ID# BAT085

# Overview

## Timeline

- This project was recompeted in FY15 and renewed in FY16.
- This project is 70% complete

## Barriers Addressed

- Inadequate Lithium and Li-ion battery energy and power density, and calendar/cycle lifetimes for PHV and EV applications
- High cell/electrode/interface impedance that limits power and affects system safety

## Budget

- FY19 funding $320k
- FY18 funding $440K
- FY17 funding $440K
- FY16 funding $440K

## Partners

- ABMR Research Groups
  - ANL, LBNL, SUNY, UP, HQ, NREL, URI, UM and UU
  - G. Chen, V. Battaglia, M. Doeff, K. Persson, V. Zorba, W. Yang,C. Martin, C. Ban, B. McCloskey
  - ALS, H. Bechtel, E . Crumlin
- UCL (UK), P. Shearing
- University of Liverpool (UK). L. Hardwick
- Central Laser Facility, Research Complex at Harwell (UK)
- Umicore, Farasis Energy, Inc.

# Relevance: Objectives

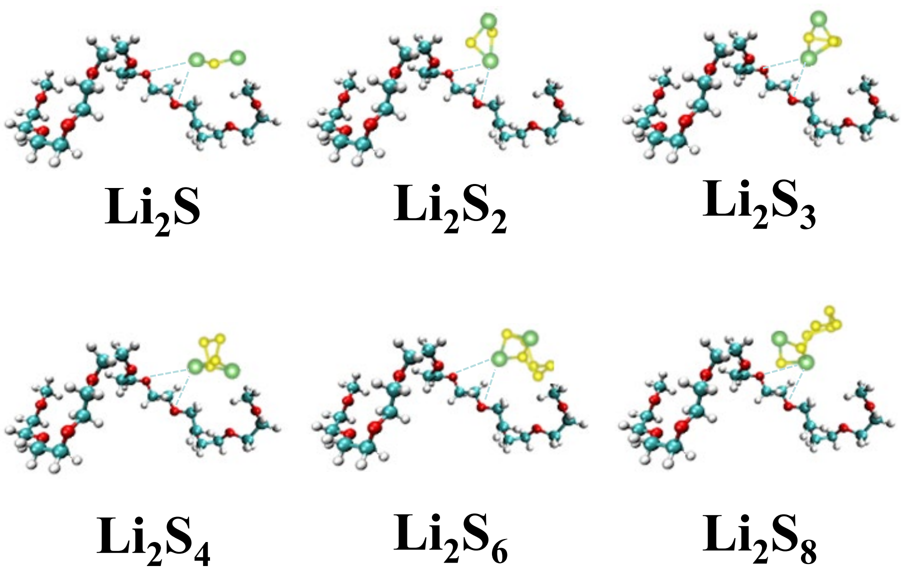
1. Apply *in situ* and *ex situ* x-ray and optical far- and near-field optical multifunctional probes to obtain detailed insight into the active material structure and the physio-chemical phenomena at electrode/electrolyte interfaces at a spatial resolution that corresponds to the size of basic chemical or structural building blocks.
2. Design new diagnostic techniques and experimental methodologies that are capable to unveil the structure and reactivity at hidden or buried interfaces and interphases that determine material, composite electrode and full cell electrochemical performance and failure modes.
3. Understand the mechanism of operation and degradation of high energy density materials for rechargeable batteries for PHEV and EV applications.
4. Propose effective remedies to address Inadequate Li-metal based battery calendar/cycle lifetimes for PHV and EV applications

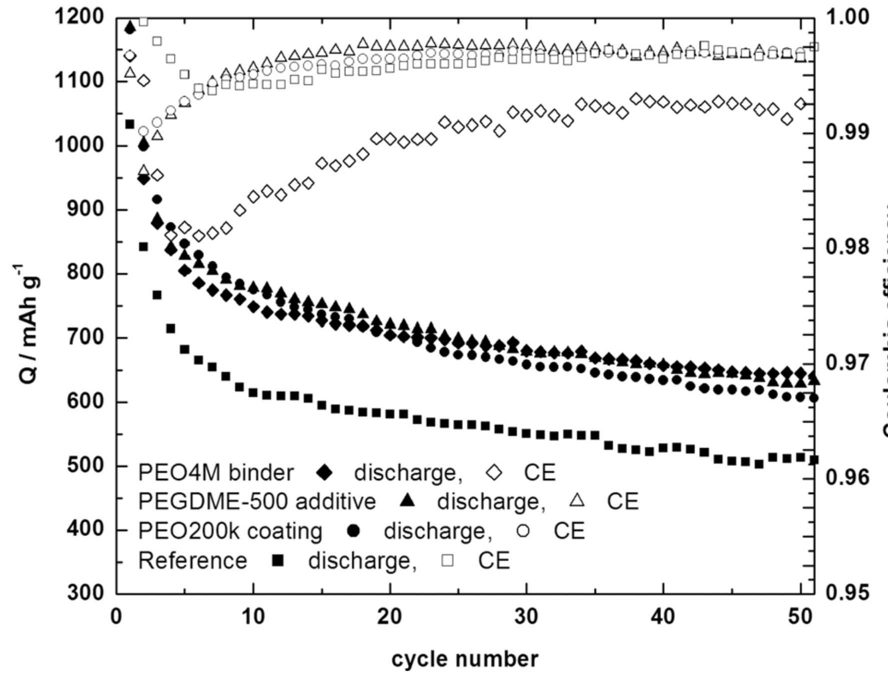
# Approach

- Develop, apply and couple advanced characterization techniques, such as optical and scanning probe spectroscopy and microscopy with standard electrochemical methods to determine function, operation and degradation of materials, electrodes and battery cells.
  - Design and develop new XAS/XPS experimental setup to characterize in situ solid/solid (e.g., NMC/SSE Li/SSE) interfaces.
  - Characterize the chemistry of solid-state electrolyte/Li and electrolyte/cathode interfaces with *ex situ* and *in situ* near field IR, XAS and XPS.
- Manufacture thin-film and composite electrode/electrolyte model systems for fundamental electrochemical studies of interfacial phenomena in Li-metal battery systems.
  - Characterize the bulk and surface structure of Li anode, NMC cathode electrodes and liquid and solid-state electrolytes and its relation to electrochemical and interfacial properties.
- Work closely with other investigators in the ABMR Program to support development of new electrode materials for high-energy Li-metal based rechargeable cells.

# Study of New Co-Block Polymer Binders for Li-S Batteries

## Background

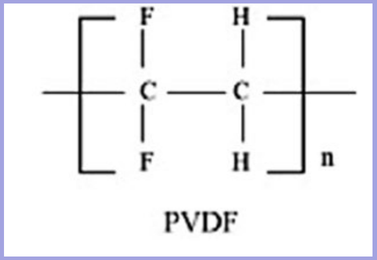
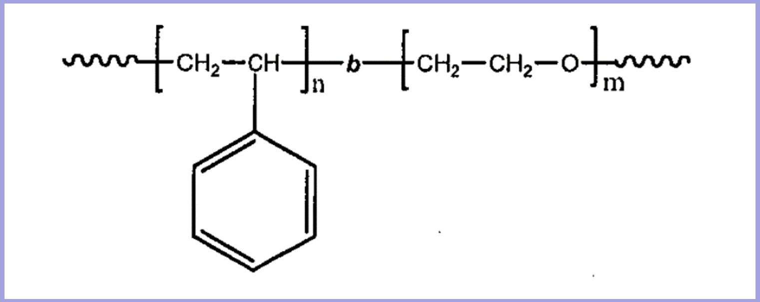



- Hydrophilicity of PEO can promote local binding with Li-polysulfides, which can confine these intermediates compunds in the cathode and inhibit active material loss.
- PEO can also dissolved in glyme-based electrolytes e.g., 1,2-dimethoxyethane (DME):1,3-dioxolane (DOL) (1:1, vol).

Matthew J. Lacey, et al., Chem. Commun., 2013,49, 8531-8533
Xiulei Ji, et al., Nature Materials, 2009, 8, 500–506

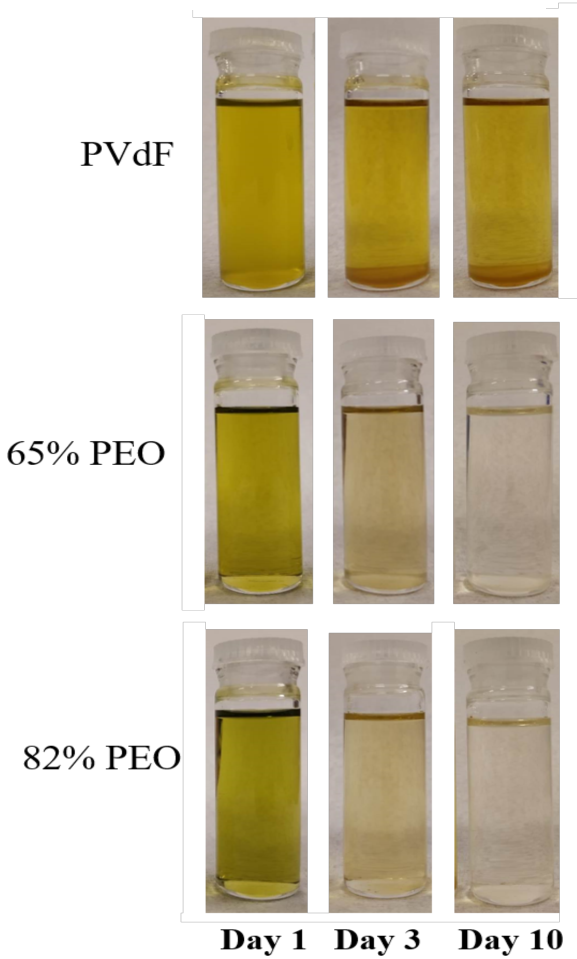
# Study of New Co-Block Polymer Binders for Li-S Batteries
## Approach

| Sample | Ref. PVdF | Block Copolymer 1801 (Polymer Source, Inc) | Block Copolymer 40890 (Polymer Source, Inc) |
|---|---|---|---|
| Chain Structure |   |  | |
| Weight % of aliphatic chain | 100% | 82% | 65% |

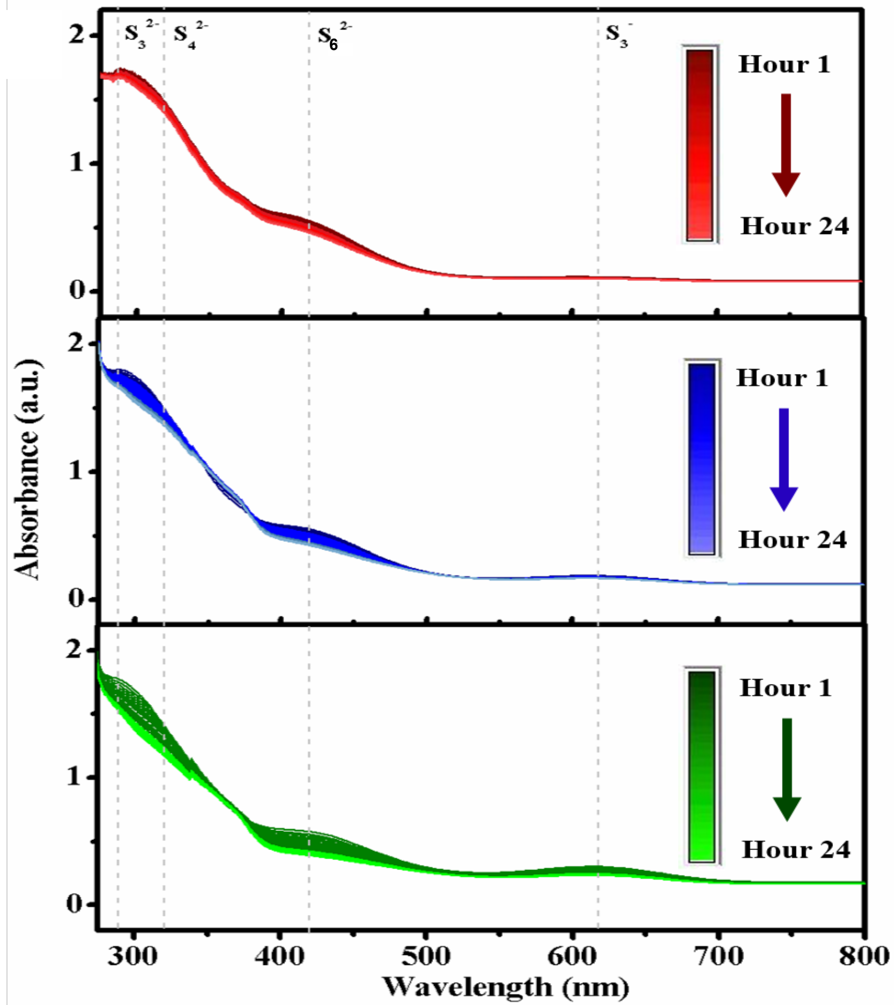
- Substitute part of the ethylene oxide unit with polystyrene to prevent dissolution of PEO-$Li_2S_x$ clusters in the electrolyte.
- Assure good mechanical properties of the binder in the composite electrode.

# Study of New Co-Block Polymer Binders for Li-S Batteries
## Proof of Concept

0.02g of binder was added to 5 ml 5 mmol Li polysulfides solution in DOL/DME(1/1 vol.)



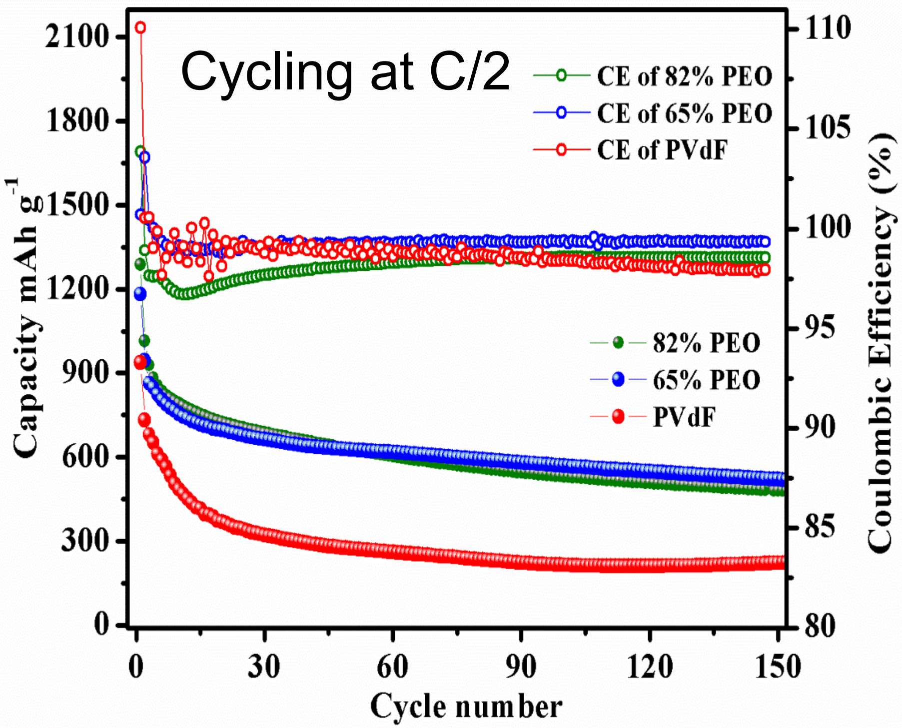

UV-Vis Spectroscopy

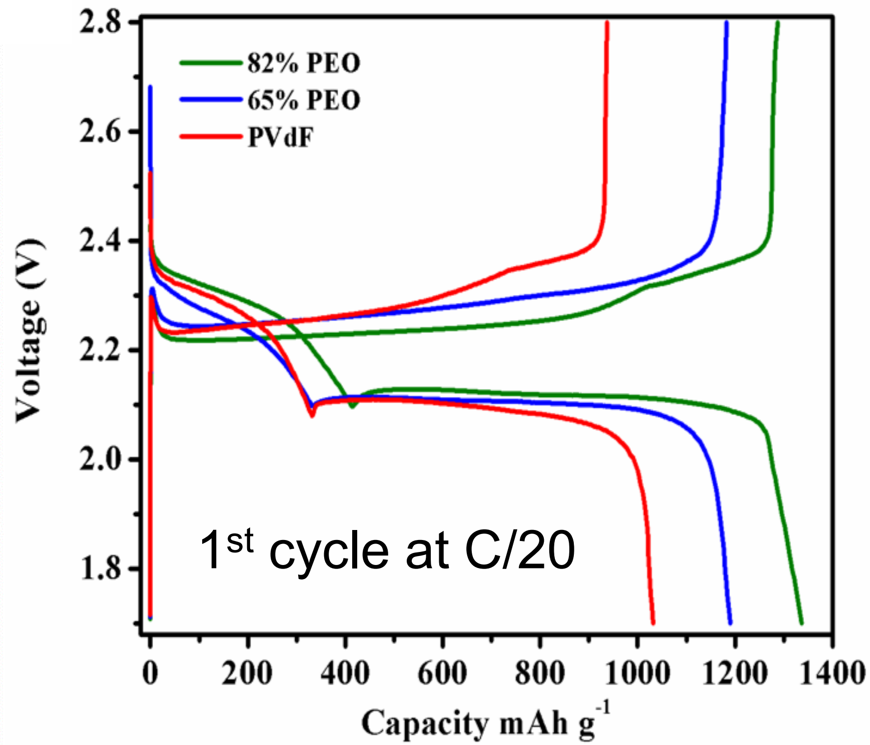



Ethylene oxide unit in co-block polymer binds with polysulfides.

# Study of New Co-Block Polymer Binders for Li-S Batteries

## Electrochemical Testing



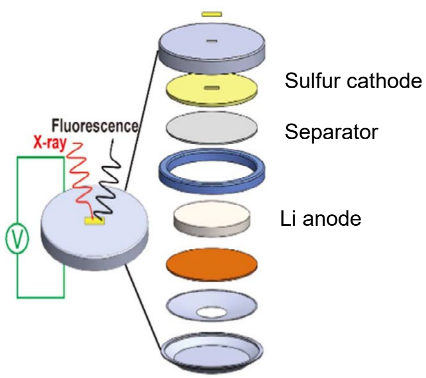




2032 coin cell equiped with composite cathode C:S:binder 0.3:0.56:0.1, 50 µl 1M LiTFSI and 2% $LiNO_3$ in DOL/DME electrolyte, Celgard 2325 separator, Li-foil anode

The sulfur composite cathode with PEO-PS (65:35 wt%) binder shows the improved capacity retention. Lower irreversible capacity loss, and higher coulombic efficiency ca. 99.6% vs. PVdF and PEO-PS (85:15 wt%) electrodes after 150 cycles.

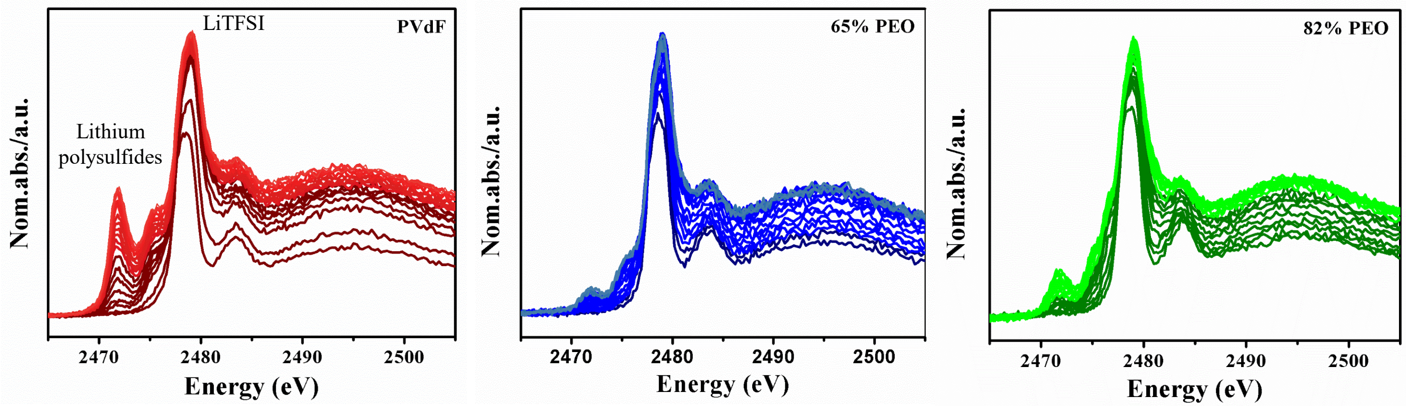
# Study of New Co-Block Polymer Binders for Li-S Batteries

*In Situ* XAS Cell



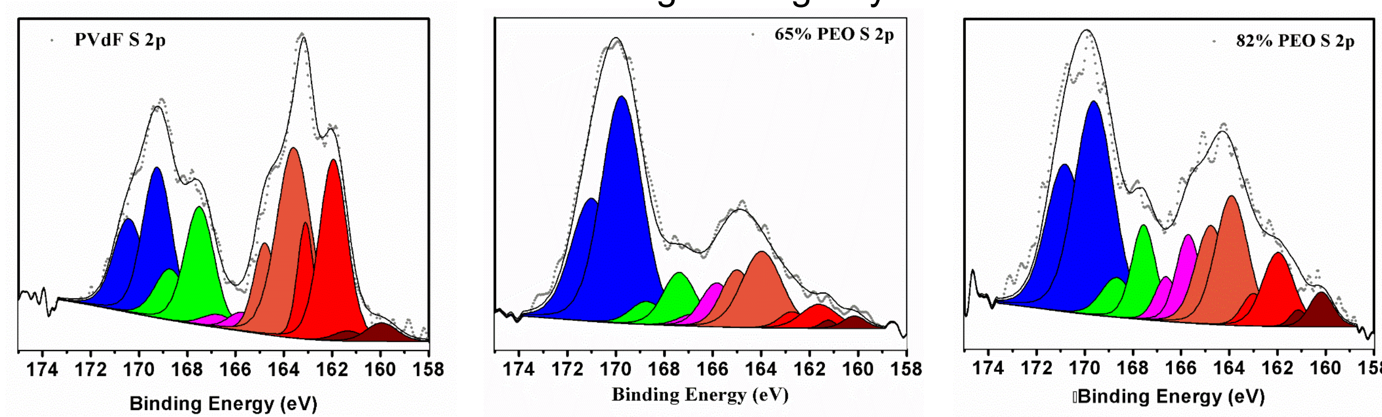

## *In operando* X-Ray Absorption Spectroscopy

1st Discharge-Charge Cycle at C/5




## *Ex situ* X-Ray Photoelectron Spectroscopy

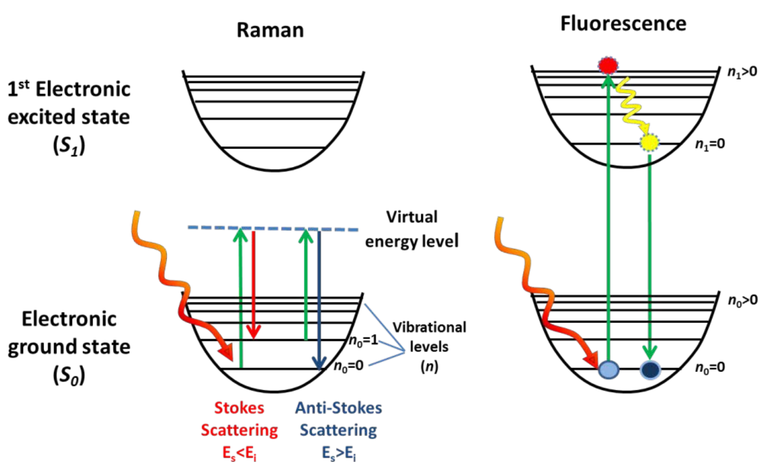
After 1st Discharge-Charge Cycle at C/5

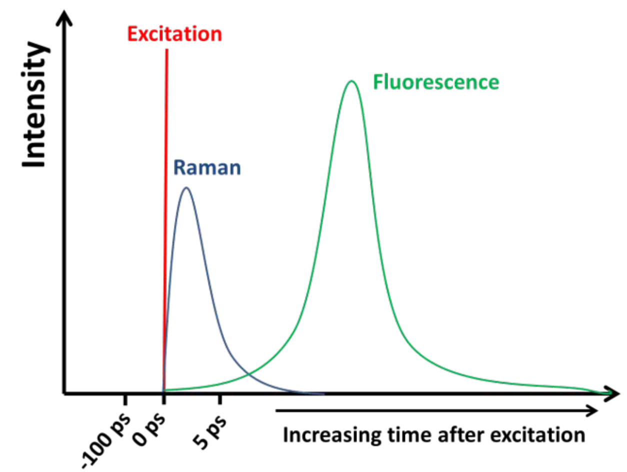


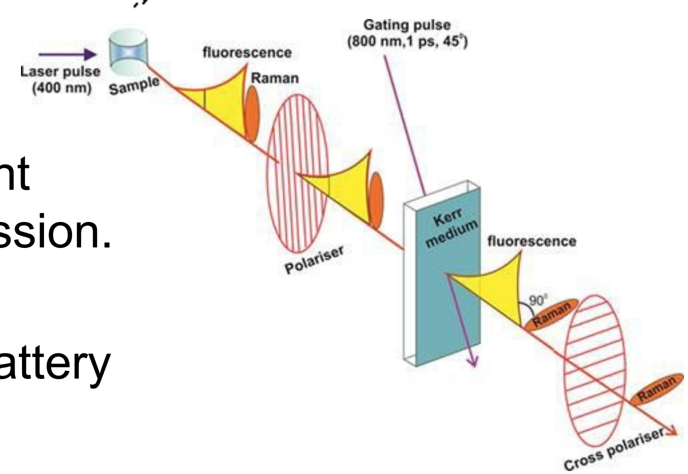

Sulfur K-edge XAS and XPS measurements of the electrolyte and Li-anode reveal that the presence of PEO-PS (65:35 wt%) binder in the sulfur composite cathode suppresses lithium polysulfides formation and dissolution.

# Kerr-Gated Raman Spectroscopy of Fluorescent Species in Li and Li-ion Batteries

- *Fluorescent species are formed during cycling of Li and Li-ion batteries as a result of electrolyte decomposition at the electrode surface.*
- *Strong fluorescence background makes it harder to analyze data due to the spectroscopic overlap of Raman scattering and fluorescence.*



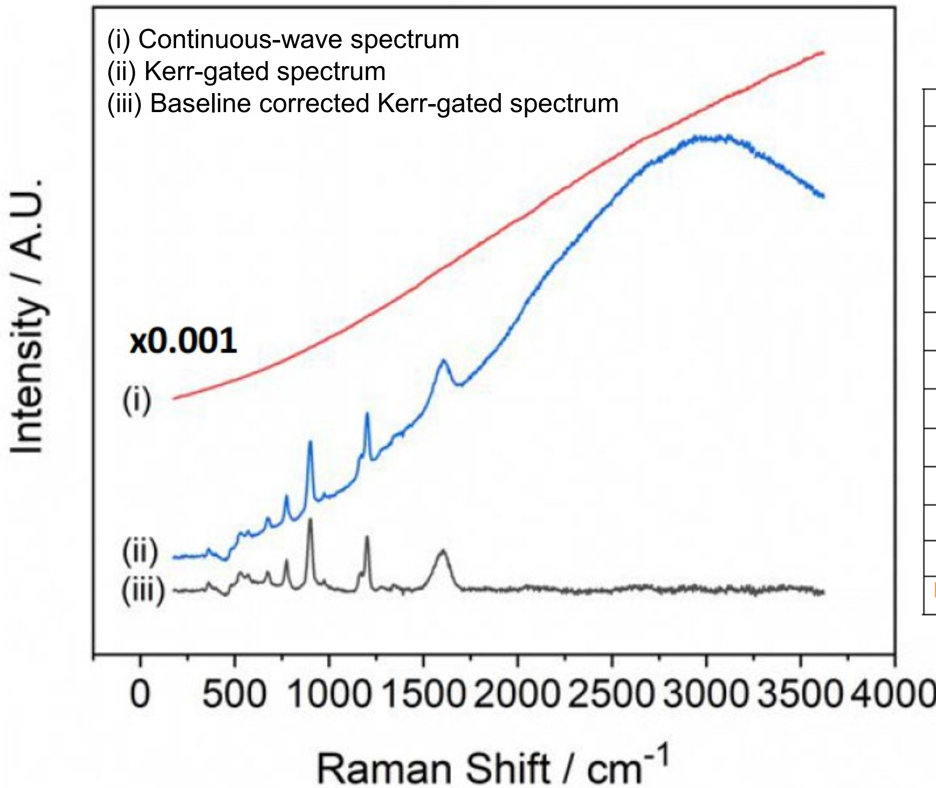




Kerr gate Raman has been proven to be an efficient technique for the suppression of fluorescence emission.

It has never been used to mitigate fluorescence background from Raman studies of Li and Li-ion battery electrode materials and interfaces.

# Kerr-Gated Raman Spectroscopy of Fluorescent Species in Li and Li-ion Batteries

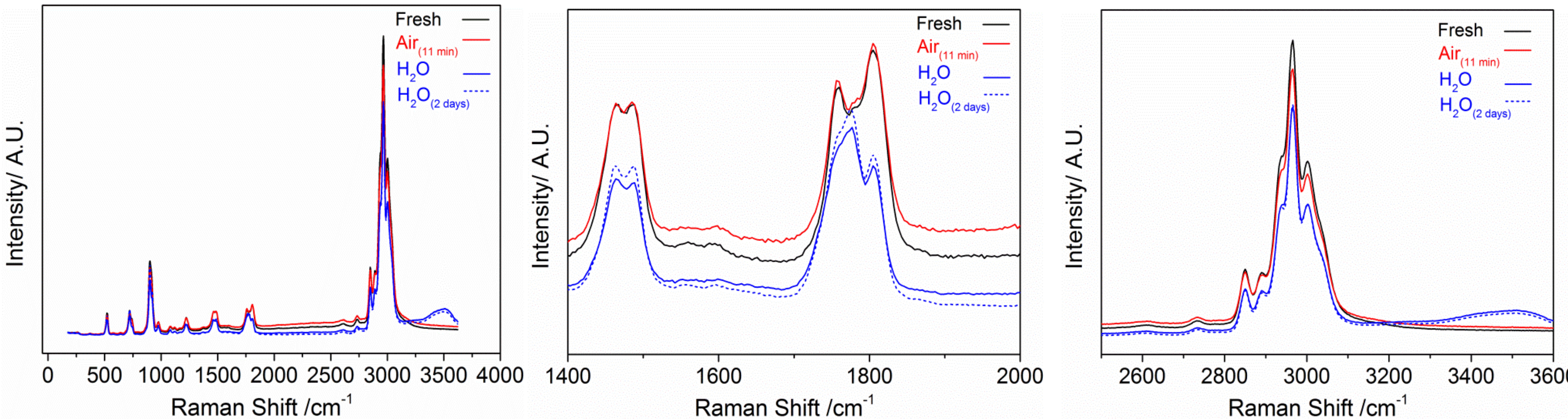



| Peak | Position/ $cm^{-1}$ | Assignment |
|---|---|---|
| 1 | 365 | $\delta(PF_3)$: $POF_3$ |
| 2 | 481 | $\delta(PF_3)$: $POF_3$ ; $LiPF_6$ |
| 3 | 525 | $PF_5$ |
| 4 | 568 | $\delta_{as}(PO_2F)$: $[P_2O_5F_2]^{2-}$ |
| 5 | 672 | -- |
| 6 | 771 | $\delta(POP)$: $[P_2O_5F_2]^{2-}$ ; $LiPF_6$ |
| 7 | 899 | $\nu(PF_3)$: $POF_3$; $\nu(PF)$: $[P_2O_5F_2]^{2-}$ |
| 8 | 975 | $\nu_{asym}(PF_3)$: $POF_3$ |
| 9 | 1167 | $\nu_{sym}(PO_2)$: $[P_2O_5F_2]^{2-}$ |
| 10 | 1199 | $\nu_{asym}(PO_2)$: $[P_2O_5F_2]^{2-}$ |
| 11 | 1345 | -- |
| 12 | 1596 | -- |
| Notation: $\nu$: stretching; $\delta$: bending; Asym: asymmetric; Sym: symmetric | | |

Collaboration with University of Liverpool (L. Hardwick) and Central Laser Facility, Research Complex at Harwell (UK)

- The $PF_6$ peaks are observed at 480 and 770 $cm^{-1}$
- New bands at 365, 525, 568, 672, 899, 975, 1200 and 1595 $cm^{-1}$ are related to the presence of $LiPF_6$ decomposition products on the surface of pristine particles.

# Kerr-Gated Raman Spectroscopy of Fluorescent Species in Li and Li-ion Batteries




Kerr gate Raman spectra at 0 ps delay of 1 M $LiPF_6$ in EC/DMC (1:1w/w); fresh, after 11 minutes exposure to air, after addition of water and after aging for 2 days in water

- Slight shift towards higher frequencies of -C=O band in DMC from 1756 cm-1 to 1760 $cm^{-1}$ after water addition.
- -C=O EC peak broadening at 1777 $cm^{-1}$ and a decrease in the relative intensity of the peak at 1805 $cm^{-1}$.
- These changes could be tentatively associated to the coordination of the water molecule to C=O carbonate group of the solvent via hydrogen bonds.
- No evidence of EC hydrolysis was observed (as suggested in literature).

Collaboration with University of Liverpool (L. Hardwick) and Central Laser Facility, Research Complex at Harwell (UK)

# Summary

1. Ethylene oxide-polystyrene co-block polymer binders can prevent dissolution of Li-polysulfides in the electrolyte and help improve long-term electrochemical performance of Li-S batteries.

    - 65% ethylene oxide unit co-block polymer binder inhibits Li-polysufides dissolution and maintain mechanical integrity of the sulfur cathode during cycling.

    - High content of ethylene oxide (82%) in the co-block polymer lead to dissolution of the binder and  Li-polysulfides into electrolyte and its accumulation on the surface of Li-anode.

2. Carried out proof-of-concept Kerr gated Raman experiments to investigate electrolyte degradation processes Li and Li-ion batteries.

    - The present study shows for the first time that Kerr gate Raman can be applied *ex situ* or *in situ* in the investigation of electrode/electrolyte interfaces of battery systems even in the presence of fluorescent species formed during cycling.

# Proposed Future Research

- *Control of the interfacial chemistry of the electrodes in lithium batteries is vitally important to their safe and effective application.*
- *The entire lithium electrode can be completely consumed by reactions with the solvent if the interfacial chemistry does not form self-limiting passive film.*
- *No effective remedy to these problems have been developed despite intense empirical effort to achieve it.*

## Approach

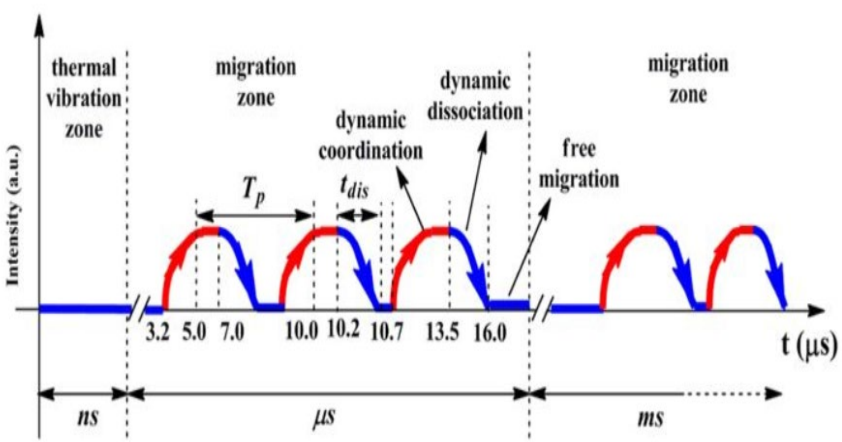
- Eliminate the effect of adventitious impurities in the electrolyte and uncontrolled surface layer on lithium foil.
    - Pre-form a surface film on metallic lithium that would be superior to the film formed spontaneously in the electrolyte.
- Develop and apply novel innovative experimental methodologies to study and understand the basic function and mechanism of operation of materials, composite electrodes, and Li-ion cells for PHEV and EV applications.
    - Use a combination of classical electrochemical methods, spectroscopic ellipsometry and UHV methods of surface preparation and characterization.
    - Develop *in situ* XPS and Near-Field IR Spectroscopy to study Li electrode/electrolyte interface Electrode Surface Films
    - Advance beyond steady state measurements towards time-resolved measurements to understand interfacial reactions kinetics and dynamics
- Work closely with ABMR PIs and industry partners to establish clear connections between diagnostics, theory/modelling, materials synthesis, and cell development efforts.

# Technical Back-Up Slides

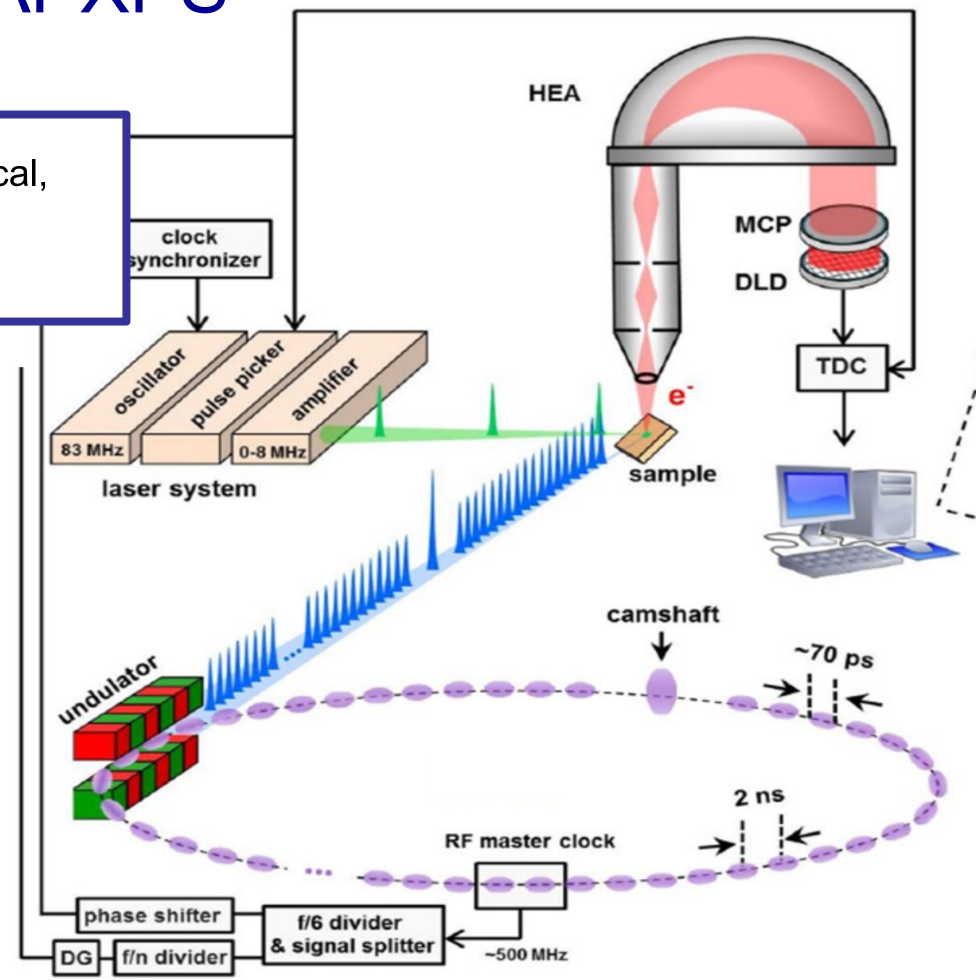
# *Need to Advance Beyond Steady State towards Time-Resolved Measurements to Understand Kinetics and Dynamics*

## Develop Time-Resolved APXPS

Electrical, Chemical,
Thermal
Pump



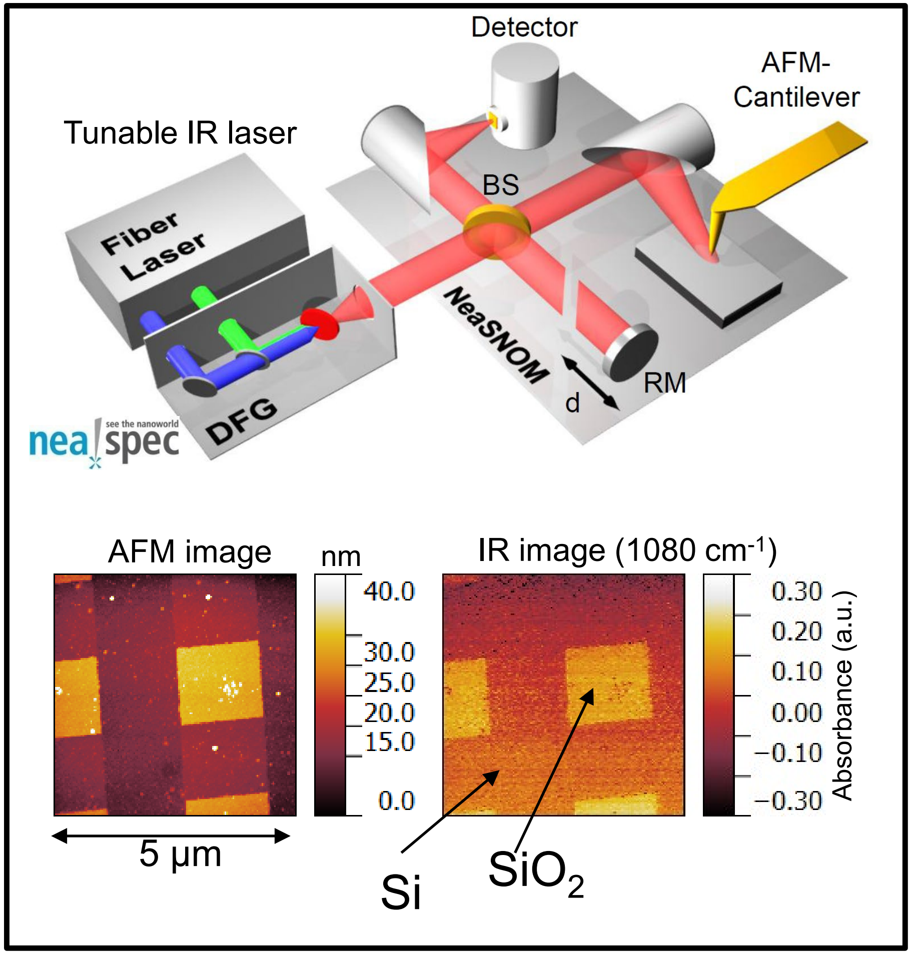

*Sci. Rep. 2017, 7, 45921.*



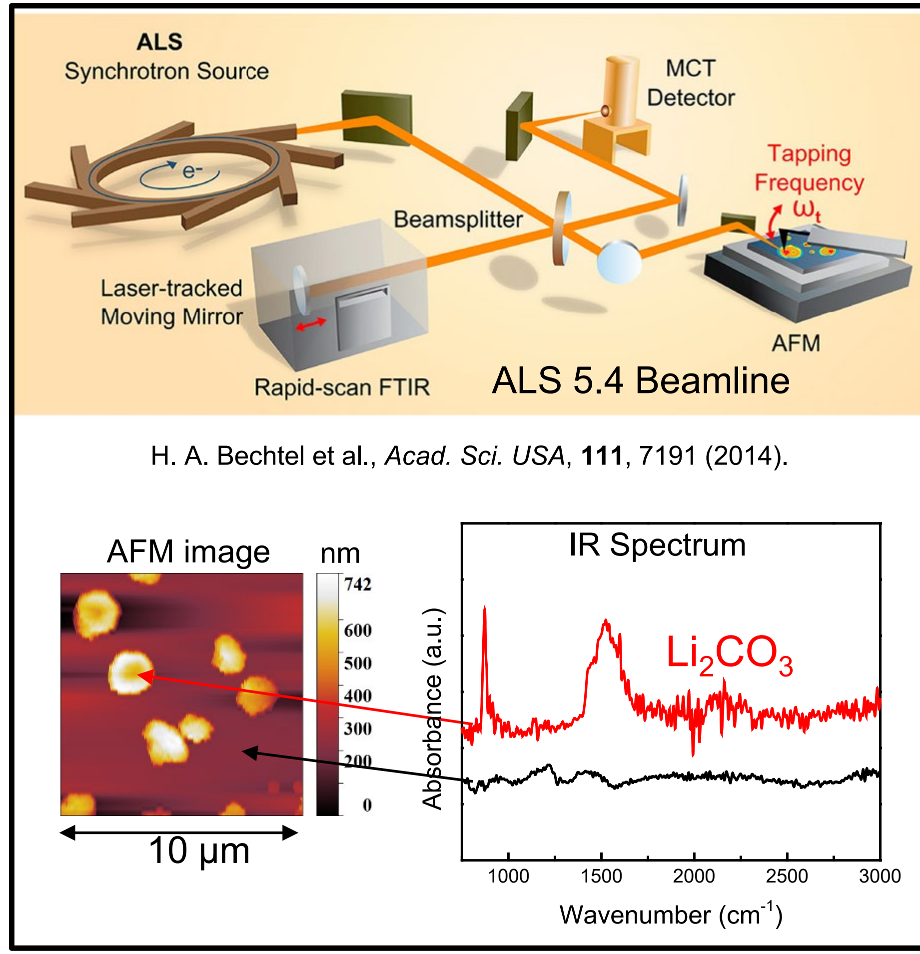

*J. Electon Spectrosc. Relat. Phenom, 200, 64, 2015*

# Apertureless Near-Field IR Microscopy/Spectroscopy

Neaspec Scattering-type Scanning Near-field Optical Microscopy (NeaSNOM)




Synchrotron Infrared Nano Spectroscopy (SINS)




- *BMR Program and LBNL have been pioneering the development and use of IR SNOM techniques to study basic phenomena in energy storage systems.*
- *We need to develop <u>in situ</u> nanoscale characterization of liquids and electrochemical interfaces with advanced NFIR techniques*